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Thermal Gravimetric Analysis of Pyrite Oxidation at Low Temperature

By J. E. Pahlman and G. W. Reimers



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	K	kelvin
°C/min	degree Celsius per minute	μm	micrometer
cm ³ /min	cubic centimeter per minute	min	minute
h	hour	mg	milligram
kcal/mol	kilocalorie per mol	pct	percent
kcal/(mol•K)	kilocalorie per mol per kelvin	vol pct	volume percent
		wt pct	weight percent

THERMAL GRAVIMETRIC ANALYSIS OF PYRITE OXIDATION AT LOW TEMPERATURE

By J. E. Pahlman¹ and G. W. Reimers²

ABSTRACT

Spontaneous oxidation and combustion of sulfides and resultant fires are serious problems in underground mines. The Bureau of Mines has conducted fundamental thermal gravimetric analysis (TGA) research to determine the mechanisms and factors governing the rate of low-temperature pyrite oxidation, and to identify possible inhibitors to spontaneous oxidation and combustion. The mechanism of low-temperature pyrite oxidation was found to be topochemical, meaning that the oxidation process is controlled by the chemical reaction at the interface between pyrite (FeS_2) and iron sulfate (FeSO_4). An activation energy of 8.9 kcal/mol FeS_2 was obtained for oxidation of minus 500-mesh pyrite in an atmosphere of 60 vol pct water vapor and 40 vol pct O_2 . Water-vapor content of the atmosphere was found to be the critical factor in the rate of spontaneous oxidation of pyrite, with a water-vapor content greater than 20 vol pct needed for accelerated oxidation. An atmosphere of pure oxygen resulted in negligible oxidation. The rate of pyrite oxidation is also greatly affected by the particle size of pyrite. Pyrite-oxidation rate increased drastically for particles less than 40 μm . Room-temperature pyrophoric behavior was observed for freshly ground unoxidized pyrite (55 pct minus 5 μm) upon exposure to air. Addition of water-adsorbing materials such as activated alumina (Al_2O_3) decreased the rate of pyrite oxidation.

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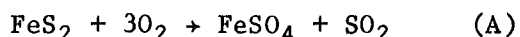
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INTRODUCTION

Although spontaneous-combustion fires comprise only about 2 pct of all metal and nonmetal fires since 1950, they comprise 47 pct of these fires lasting longer than 24 h. Spontaneous-combustion fires are quite disruptive to mine operations. In addition to the money spent on rescue and recovery efforts, equipment repair and replacement, and mine rehabilitation, mines shut down by fires are forced to forego thousands of tons of mineral production. For example, spontaneous combustion in a caved section at the Magma Copper Co., Magma Mine, Arizona, in 1961, stopped production for 2 months (1).³ Spontaneous combustion is the third leading cause of fires in non-coal underground mines and the second leading cause of fires that result in fatalities, and alone accounts for more fire deaths than all other causes combined (2).

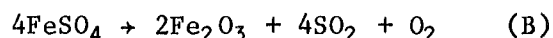
Spontaneous-combustion fires are difficult to detect because they grow slowly over an extended period of time (weeks or months), and are difficult to extinguish because they often start in sealed or abandoned sections of a mine where access for firefighters is difficult, if not impossible (3). Because of their relative inaccessibility, observations of the fire area to learn about ignition and growth mechanisms are nearly impossible. Also, because sealing or flooding of affected areas are the most used means of spontaneous-combustion fire control, post fire investigations are again difficult.

Spontaneous oxidation of sulfides results in the generation of large quantities of heat. For instance, oxidation of pyrite (FeS_2) to ferrous sulfate (FeSO_4) according to the reaction

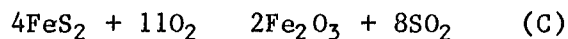


results in a liberation of 265.5 kcal/mol FeS_2 . When this heat cannot be

dissipated, temperatures can rise to the point where spontaneous combustion of both pyrite and adjacent timber and other mine combustibles may be produced. In addition to the obvious hazards of fire and increased temperatures, the generation of sulfur dioxide (SO_2), carbon monoxide (CO), and other toxic gases, along with the depletion of mine oxygen supply pose imminent dangers to the well-being of the mine workers. In more advanced stages of spontaneous combustion, temperatures can rise to the point where the FeSO_4 formed begins to decompose according to the reaction



or even direct oxidation of pyrite to hematite (Fe_2O_3) according to the reaction



occurs with the evolution of significant quantities of SO_2 and, in extreme cases, hot mists of H_2SO_3 . If timber is present in the area of pyrite oxidation, more toxic CO or CO_2 will be liberated depending upon whether there is sufficient air to support complete combustion.

Ninteman (4) provides a comprehensive overview of the complex nature and problems associated with spontaneous oxidation and combustion of sulfide ores in underground mines. Although the mechanism of sulfide oxidation is highly complex and not well-known, the qualitative effects of several variables are known. Iron sulfides are the most reactive of the sulfides. Reactivity of the sulfides is increased when more than one type of sulfide is present. Greater sulfide concentration results in greater heat production. Although water vapor catalyzes the oxidation, in excess it acts to cool the sulfides and reduce the oxidation rate. The structure of the ore is also important. Highly-fractured or porous structures allow oxygen to penetrate to more sulfide surfaces. The presence of

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

lower ignition point combustibles, such as timbers or refuse, in contact with oxidizing sulfides seriously increases the danger of spontaneous combustion and ensuing fire. The precise interrelationships of these factors, though essential for effective prevention and control, are unknown.

The object of the present investigation was to conduct a fundamental study of the

low-temperature oxidation of pyrite to determine the mechanism and the inter-relationship between variables such as water-vapor content and oxygen content of the atmosphere and pyrite particle size. Pyrite was chosen as the candidate sulfide for this investigation because of its abundant occurrence in most sulfide deposits.

SAMPLE PREPARATION

The pyrite sample used in this investigation was from Colorado and was obtained through a mineral supply company. An X-ray analysis of the sample indicated that it was almost pure pyrite with some quartz and some chalcopyrite. Chemical analysis of the sample indicated the presence of 51.6 wt pct S, 46.7 wt pct Fe, 1.6 wt pct SiO_2 , and 0.1 wt pct Cu.

The "as-received" pyrite sample was coarse ground to minus 1/8 in, using small crushers. The minus 1/8 in plus 100-mesh fraction was ground to minus 100

mesh in a rod mill, and wet screened to give minus 100- plus 150-, minus 150- plus 200-, minus 200- plus 270-, minus 270- plus 325-, minus 325- plus 400-, minus 400- plus 500-, and minus 500-mesh fractions. Oversize (plus 100 mesh) was reground in the rod mill. Screened samples were dried under nitrogen atmosphere, and stored under an argon atmosphere. Comparison of the chemical analyses of each size fraction indicated that there was no sample deterioration due to grinding.

EXPERIMENTAL APPARATUS AND PROCEDURE

Weight-change measurements were made using a Perkin-Elmer⁴ thermal-gravimetric-analysis (TGA) apparatus. The apparatus consists of an electrobalance unit, a furnace element, a thermocouple, a tare pan, a sample pan, and a provision for conducting tests under a flowing-gas atmosphere (fig. 1). The 40-mg pyrite samples were placed in the sample pan, suspended from the balance, and entered into the cylindrical furnace unit just above the thermocouple. The sample weight was roughly tared out by placing weights in the tare pan, and exactly tared out using an "electronic tare." As the sample was heated to the desired temperature, a flow of nitrogen gas through the sample chamber was maintained using the gas inlet and outlet tubes. Oxygen was scrubbed from the nitrogen stream by

passing it over hot (500° C) copper turnings before entering the sample chamber. Heating of the sample was accomplished by using a programmable controller. The sample temperature was measured by the thermocouple. When the desired temperature was reached, the test gas consisting of oxygen, water vapor, and/or nitrogen was flowed through the sample chamber. The desired water-vapor content of the test gas was reached by bubbling dry oxygen gas (O_2) and/or nitrogen (N_2) gas through a flask of heated distilled water. The amount of water vapor picked up was a function of the dry gas flow and the temperature of the water bath. Weight-change data were obtained either as a function of temperature or as a function of time. These data were recorded on a thermal-analysis-data-station (TADS) unit where they were stored for future manipulation and plotting on a graphical plotter.

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

PYRITE OXIDATION RESULTS

EFFECT OF TEMPERATURE

The effect of temperature on the oxidation of pyrite was investigated first. Although mine temperatures are normally below 50° C, the rate of pyrite oxidation at those temperatures is too slow to be measured in a reasonable amount of time. Thus, laboratory experiments had to be conducted at temperatures at which a measurable amount of oxidation takes place in a reasonable amount of time. Tests were conducted at 100°, 150°, 175°, 200°, 225°, 250°, 275°, 300°, 315°, 320°,

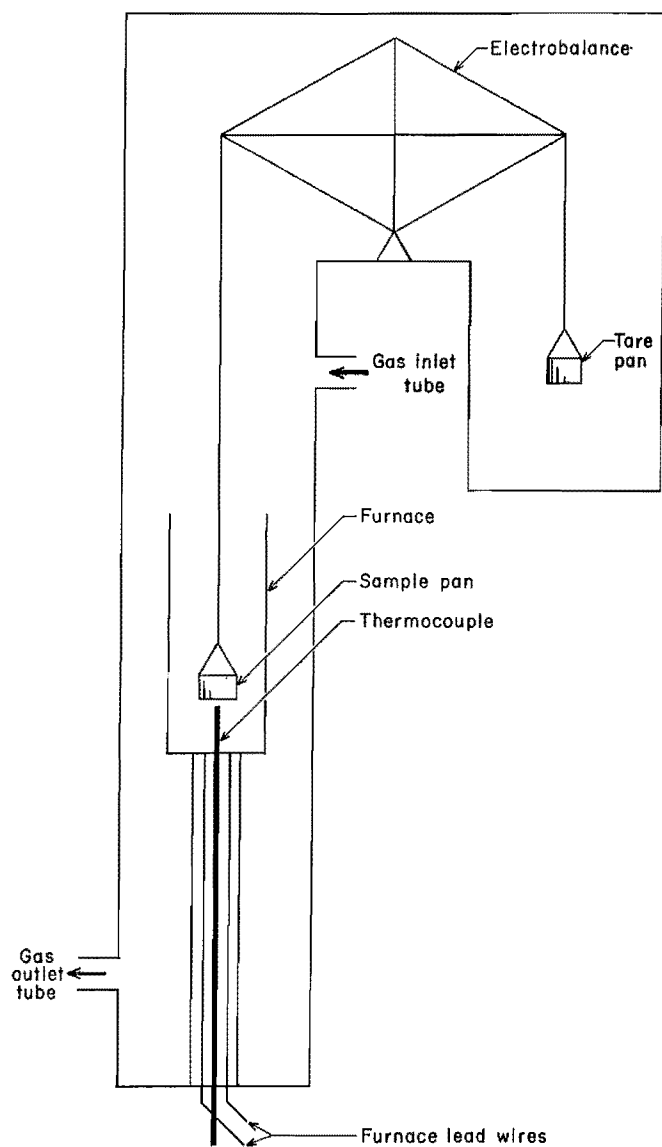


FIGURE 1.—Schematic diagram of TGA apparatus.

325°, and 350° C. For clarity, figure 2 shows only plots of the pct total pyrite oxidation versus time for the temperatures of 100°, 150°, 175°, 200°, and 300° C. In all tests, an atmosphere containing 40 vol pct O_2 and 60 vol pct water vapor was flowed over the minus 500-mesh sample at a rate of 500 cm^3/min .

At 100° C, slight oxidation was observed in 5 h. From 150° to 175° to 200° C, the extent of oxidation increased with the maximum-oxidation rate occurring at 200° C. This means that the optimum temperature for pyrite oxidation is also the temperature at which wood begins to burn (200° C). Only $FeSO_4$ formation occurs during pyrite oxidation at these four temperatures, as is evidenced by petrographic analyses of these samples, which showed only the presence of unreacted FeS_2 and $FeSO_4$. At 225° C, the rate of weight gain started to slow after an initial period of increased weight gain. This indicated that although pyrite oxidation was faster at this temperature, $FeSO_4$ decomposition began after an initial period of formation. The $FeSO_4$ decomposition in this sample and those oxidized at temperatures up to 320° C was substantiated by petrographic analyses of these samples. Both $FeSO_4$ and Fe_2O_3 were present in these samples, together with unreacted FeS_2 . The combination of an increased weight gain due to sulfate formation with a weight loss due to sulfate decomposition resulted in a net decrease in the weight-gain rate. At 250° and 275° C, the rates of pyrite oxidation and $FeSO_4$ decomposition were observed to be equal after about 60 min of $FeSO_4$ formation (no net weight gain or loss). At 300° (fig. 2), 315°, and 320° C, the rate of sulfate decomposition was greater than its rate of formation, and a weight loss was observed after an initial net weight gain. At 325° and 350° C, immediate weight losses were observed, indicating that pyrite was oxidized directly to hematite. Petrographic analysis of these samples substantiate this conclusion, as only unreacted FeS_2 and Fe_2O_3 were present in these samples.

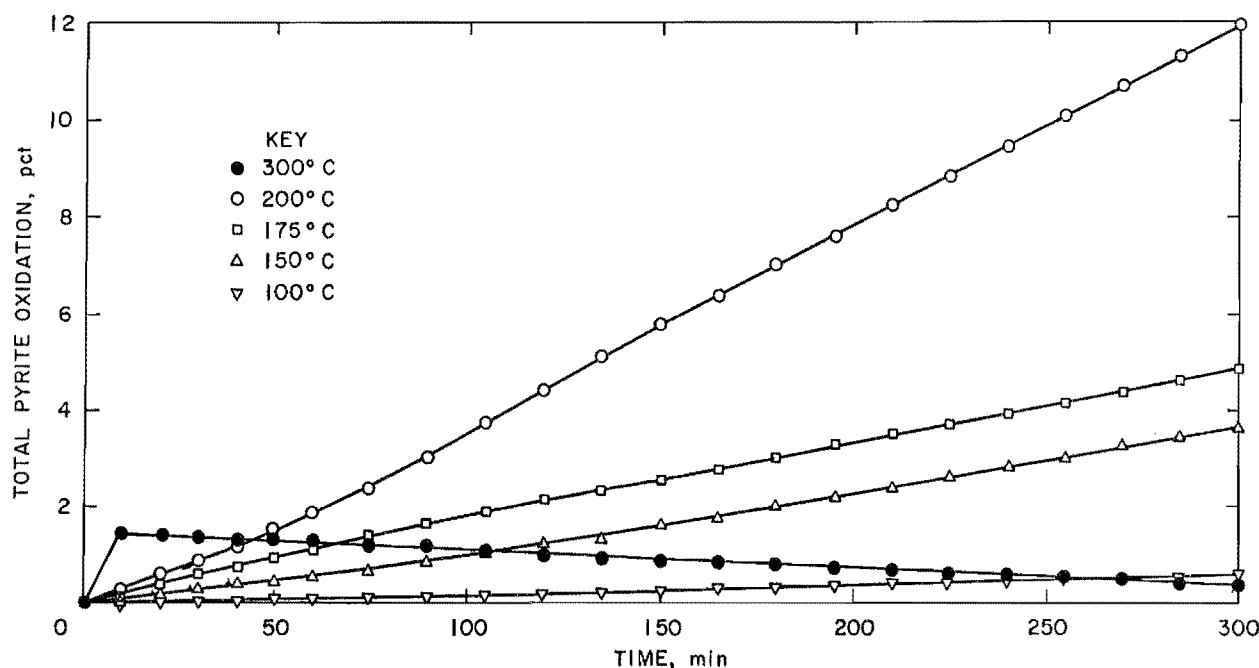


FIGURE 2.—Effect of temperature on pyrite oxidation.

Since at 200° C, the highest rate of weight gain (oxidation) was observed without an accompanying weight loss due to sulfate decomposition, it was picked as the temperature at which to conduct other pyrite-oxidation tests. It should be noted that the temperature at which sulfate decomposition, and therefore increased SO₂ production, begins (225° C) is above the initiation temperature for wood burning (200° C). This means that measurement of SO₂ levels in a mine atmosphere would not be reliable as an early-detection system for spontaneous-combustion fires. A fire could be well started before an SO₂ level increase is observed.

EFFECT OF WATER VAPOR AND OXYGEN

The effect of water-vapor content of the atmosphere on pyrite oxidation is quite dramatic. Figure 3 is a plot of the total pyrite oxidation versus water vapor in the gas atmosphere flowing past the sample. For these tests, the oxygen content was kept constant at 40 vol pct while the water-vapor content varied from 0 to 60 vol pct, and the nitrogen content correspondingly varied from 60 to 0 vol pct. The

presence of up to 20 vol pct water vapor resulted in a very small increase in oxidation at 200° C in 4 h; however, increasing the water-vapor content above 20 vol pct resulted in a drastic increase in the amount of pyrite oxidation in 4 h. On the basis of these data, the water-vapor content should be kept below 20 vol pct to retard pyrite oxidation.

Although pyrite oxidation requires the presence of some oxygen in the atmosphere, oxygen content is not the critical factor in spontaneous oxidation of pyrite. In the absence of water vapor, variation in oxygen contents of 30, 40, 60, and 100 vol pct did not result in measurable oxidation. To determine the effect of oxygen content of the atmosphere on pyrite oxidation, water-vapor content was kept constant at 40 vol pct, the oxygen content was varied from 0 to 60 vol pct, and the nitrogen content was correspondingly varied from 60 to 0 vol pct in 4-h tests. The results are shown in figure 4. Measurable oxidation was obtained with as little as 5 vol pct O₂ with the presence of 40 vol pct water vapor. The rate of pyrite oxidation was found to increase with increasing oxygen content of the atmosphere up to about 30 vol pct O₂. Atmospheres with higher

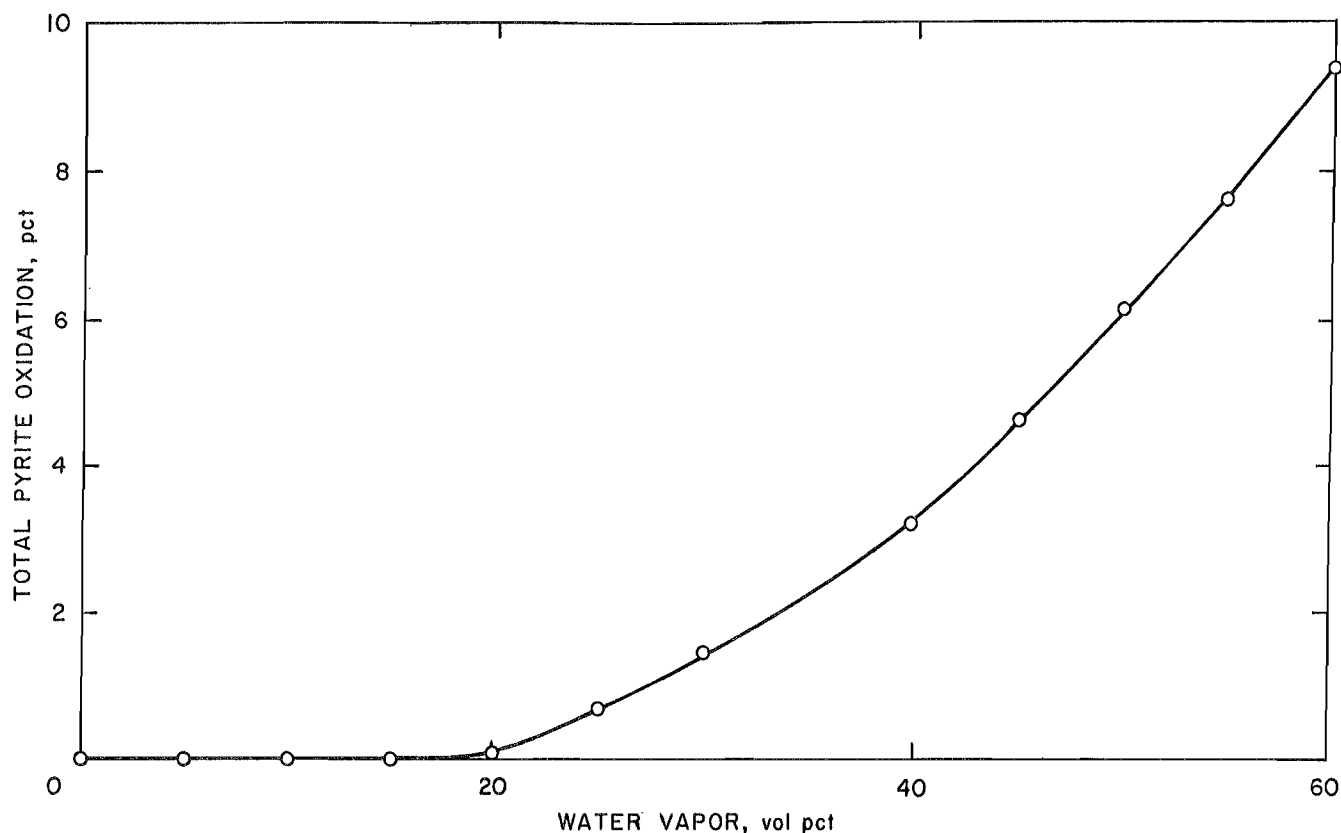


FIGURE 3.—Effect of water-vapor content on pyrite oxidation.

oxygen contents did not result in further increases in the rate of pyrite oxidation. Based on these data, it is concluded that water-vapor content and not oxygen content is the critical factor in pyrite oxidation. Apparently, water molecules adsorbed on the pyrite surface greatly enhance the reaction of oxygen from the atmosphere with the sulfur in the pyrite, and thus increase the rate of pyrite oxidation. The number of water molecules on the surface is proportional to the water-vapor content of the atmosphere.

Backfilling of mined-out areas with "wet" pyrite-containing tailings and sealing off the areas initially retards pyrite oxidation since oxygen is in limited supply and the excess water has a cooling effect on any oxidizing pyrite. When the seals crack enough to allow the tailings to dry out and equilibrate with the atmosphere so that the atmosphere contains at least 20 to 60 vol pct water vapor, the pyrite in the tailings will begin to quickly oxidize and self-heat.

If carbonaceous material is present, it can be set on fire. Water is also commonly used to suppress spontaneous-combustion fires. This does not mean, however, that the sulfides will not spontaneously reignite when the pyrite again begins to dry out and the humidity level is again in the critical range.

The importance of water vapor in sulfate formation was also shown in other experiments. In these tests, minus 500-mesh pyrite samples were heated to 200° C under nitrogen, and then soaked at 200° C for 2 h in an atmosphere containing either 40 vol pct O₂ and 60 vol pct N₂ or 40 vol pct O₂, 20 vol pct N₂, and 40 vol pct water vapor. After 2 h, the atmospheres were switched. The sample that initially was not subjected to water vapor neither gained weight (sulfate formation) nor lost weight (hematite formation) in the first 2 h. However, with the introduction of water vapor after 2 h, pyrite was oxidized to sulfate as evidenced by a weight gain. The sample that initially was subjected to water

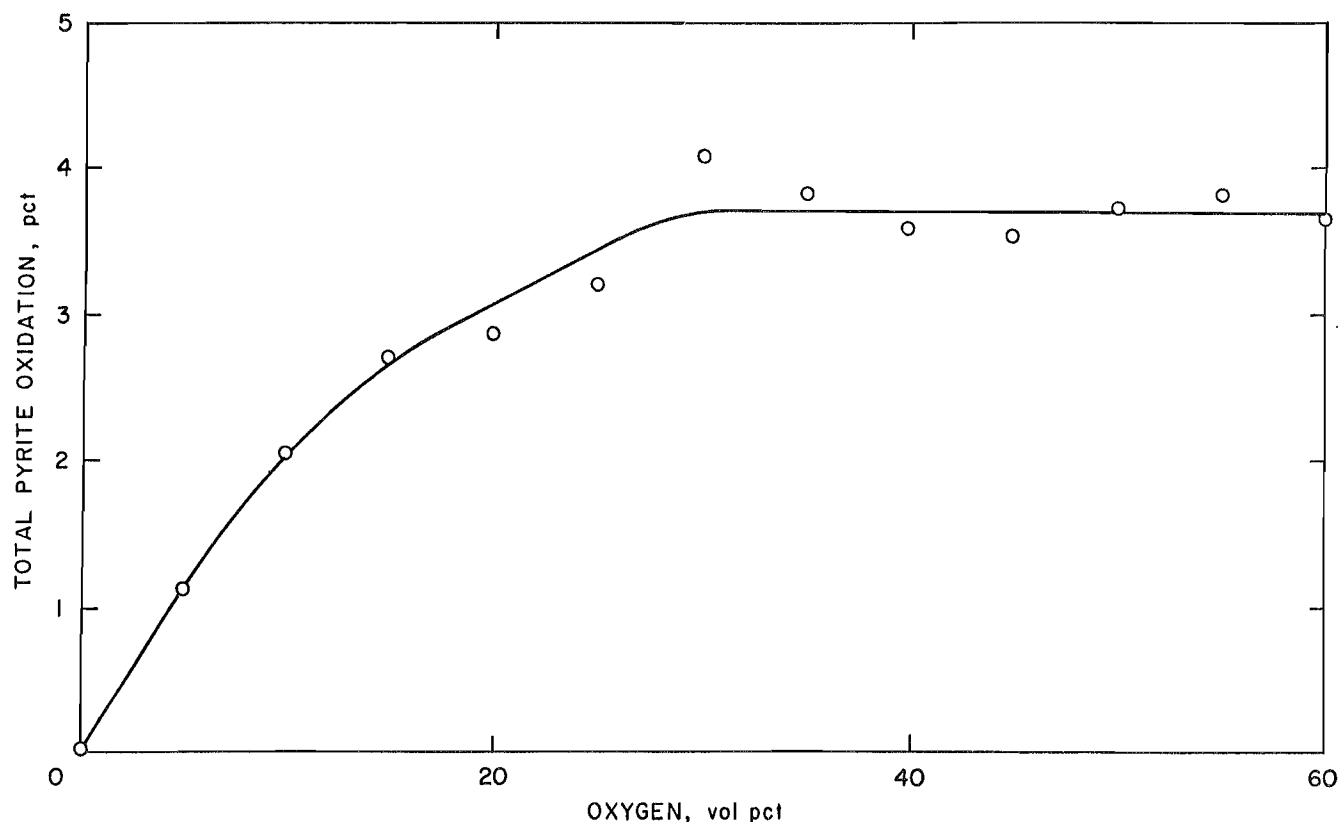


FIGURE 4.—Effect of oxygen content on pyrite oxidation.

vapor gained weight (sulfate formation) in the first 2 h. When water vapor was no longer introduced after 2 h, no additional weight gain or loss was observed.

Water vapor in the atmosphere also raises the temperature at which direct oxidation to Fe_2O_3 is observed. Samples of minus 500-mesh pyrite were heated from 100° to 400°C at a rate of $5^\circ\text{C}/\text{min}$ in an atmosphere containing 40 vol pct O_2 and 60 vol pct N_2 , as well as in an atmosphere containing 40 vol pct O_2 , 20 vol pct N_2 , and 40 vol pct water vapor. With no water vapor present, pyrite oxidation was not observed (neither sulfate formation nor oxide formation) until the sample temperature reached about 325°C . At this temperature, a drastic weight loss was observed owing to direct oxidation of pyrite to Fe_2O_3 . With water vapor present, an increasing weight gain (sulfate formation) was observed until about 360°C where the drastic weight loss was again observed.

EFFECT ON PARTICLE SIZE

The effect of particle size on low-temperature pyrite oxidation is quite dramatic. Figure 5 is a plot of the pct total oxidation versus time for minus 325- plus 400-, minus 400- plus 500-, and minus 500-mesh samples of pyrite. Also tested were minus 100- plus 200-, minus 200- plus 270-, and minus 270- plus 325-mesh samples, but they resulted in negligible pyrite oxidation in 6 h under an atmosphere of 40 vol pct O_2 and 60 vol pct water vapor at 200°C . Under identical conditions minus 325- plus 400-, minus 400- plus 500-, and minus 500-mesh pyrite particles were 0.15, 10.0, and 14.5 pct oxidized at the end of 6 h. Since most sulfide ore beneficiation tailings would contain from 50 to 70 pct minus 400-mesh material that includes pyrite particles, the probability of pyrite oxidation and self-heating is high when "wet tailings" used to backfill a mined-out area begin to dry out. Agglomeration

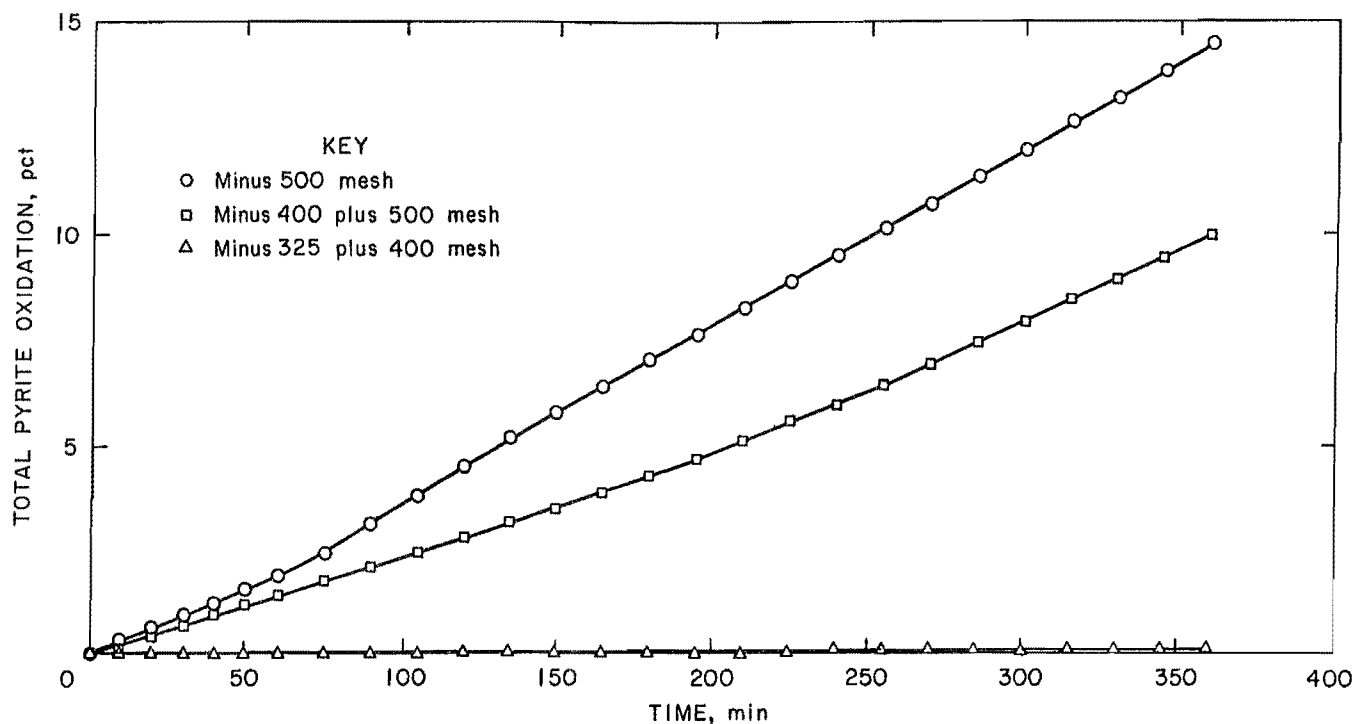


FIGURE 5.—Effect of particle size on pyrite oxidation.

of the tailings into larger-size pieces before backfilling may not be economically favorable, but still may be warranted to help retard pyrite oxidation and thus prevent mine fires. In effect, the agglomerated tailings would act like large pyrite particles, and thus oxidize at a much slower rate.

The drastic effect of particle size on oxidation of pyrite was further shown by the pyrophoric behavior of fine pyrite. Fine, unoxidized particles of pyrite were prepared by ball-milling a pyrite sample in heptane (liquid) for 2 h.

The ground product contained 55 pct minus 5 μm particles, 85 pct minus 10 μm particles, 95 pct minus 30 μm particles, and 100 pct minus 100 μm particles. A portion of this heptane-pyrite slurry was evaporated to dryness under argon. Upon exposure to air with ambient humidity, the pyrite self-ignited and spontaneously combusted with a red glow. The resultant solid was red in color, and was found to be Fe_2O_3 . Another portion of the fine-pyrite slurry was evaporated to dryness in the same manner except dry air was used instead of argon. This sample did not self-ignite when exposed to room air with ambient humidity like the

argon-dried sample did. Instead, the sample had to be heated above room temperature with a torch before it would self-ignite and spontaneously combust. It is concluded that exposure of pyrite to oxygen in the absence of water vapor has a passivating effect on pyrite. Thus, a purposeful preoxidation of pyrite surfaces with air alone may help inhibit spontaneous combustion of pyrite. The effect of particle size on self-ignition temperatures was also evaluated. Four identical pyrite samples were ground in heptane for 15, 30, 60, and 120 min, respectively, and then dried under argon. The resultant dried products contained 30, 35, 42, and 55 pct minus 5- μm particles, respectively. Samples of these dried products were heated to 400° C at a rate of 5° C/min in the TGA, and the temperatures at which these samples self-ignited and spontaneously combusted to Fe_2O_3 were determined. The self-ignition temperature in dry air decreases with increasing percentage of particles less than 5- μm -in size in the dried slurries. Observed self-ignition temperatures were 338°, 335°, 325°, and 285° C for the 15-, 30-, 60-, and 120-min ground samples.

EFFECT OF ADDITIVES

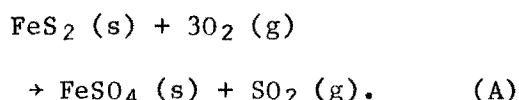
Figure 6 shows the effect of activated Al_2O_3 addition on the rate of pyrite oxidation. With minus 500-mesh pyrite alone, 14.5-pct oxidation was achieved in 6 h at 200°C in an atmosphere containing 40 vol pct O_2 and 60 vol pct water vapor. By mixing an equal weight of powdered activated Al_2O_3 with the minus 500-mesh pyrite, only 0.24-pct oxidation was achieved in 6 h under similar atmosphere. Apparently, the activated Al_2O_3 adsorbs water vapor preferentially to pyrite, and thus obviates the catalytic effect of water vapor on pyrite oxidation.

Kaolin, "nonactivated" Al_2O_3 , calcium oxide (CaO), and a water-adsorbing additive were also evaluated as pyrite-oxidation inhibitors. Kaolin and "non-activated" Al_2O_3 additions equal to the weight of the pyrite resulted in less than 10-pct decreases in the rate

of pyrite oxidation at 200°C in an atmosphere containing 40 vol pct O_2 and 60 vol pct water vapor. Addition of an equal weight of the water-adsorbing agent resulted in a decrease of 25 pct in the rate of pyrite oxidation under these same conditions. CaO additions of 20, 40, 60, 80, and 100 wt pct of pyrite resulted in increased-oxidation rates. It is concluded that additives that preferentially adsorb water can be "dusted" on "mined-out" area roofs and walls to help inhibit pyrite oxidation. Dusting "mined-out" area walls with CaO would enhance, rather than retard, pyrite oxidation. This is not unexpected since CaO is a good scavenger of sulfur-containing gases. By combining with these gaseous products, it will drive pyrite-oxidation reactions involving formation of these gases toward completion (to the right), thereby increasing the rate of pyrite oxidation.

KINETICS OF PYRITE OXIDATION

The reaction for pyrite oxidation at low temperatures ($<200^\circ\text{C}$) is as follows:



This pyrite oxidation results in the formation of a product layer of FeSO_4 around the reactant (FeS_2). The kinetics governing such a reaction depend upon whether the FeSO_4 product layer is porous or protective (nonporous). If the FeSO_4 forms a protective layer around the FeS_2 , the rate-determining step is the diffusion of the O_2 through the product layer. Assuming that the reacting particles retain a spherical geometry during the oxidation, the rate equation for diffusion is the Crank, Ginstling, and Braunshtein equation (5)

$$\begin{aligned} F_d(r) = 1 - \frac{2}{3} r \\ - (1 - r)^{2/3} = kt, \end{aligned} \quad (\text{1})$$

where r is the fraction reacted, k is the rate coefficient, and t is time.

If the FeSO_4 layer is porous enough, the rate-determining step is the chemical reaction occurring at the interface between the reactant (FeS_2) and product (FeSO_4). The rate, therefore, is directly related to the available surface area of the reactant at any time, and is termed topochemical. Again, assuming that the reacting particles retain a spherical geometry during the oxidation, the rate equation for topochemical oxidation is

$$F_+(r) = 1 - (1 - r)^{1/3} = kt, \quad (\text{2})$$

where again r is the fraction reacted, k is the rate coefficient, and t is time (6).

A linear variation of $F_d(r)$ with time would support the adherence of reaction to diffusion kinetics, while a linear variation of $F_+(r)$ with time would support the adherence of reaction to topochemical kinetics.

Variations of $r \times 100$ with time are shown in figure 2, and were computed from weight-change data. Variations of $F_+(r)$ with time are shown in figure 7. The linearity of these plots substantiates a

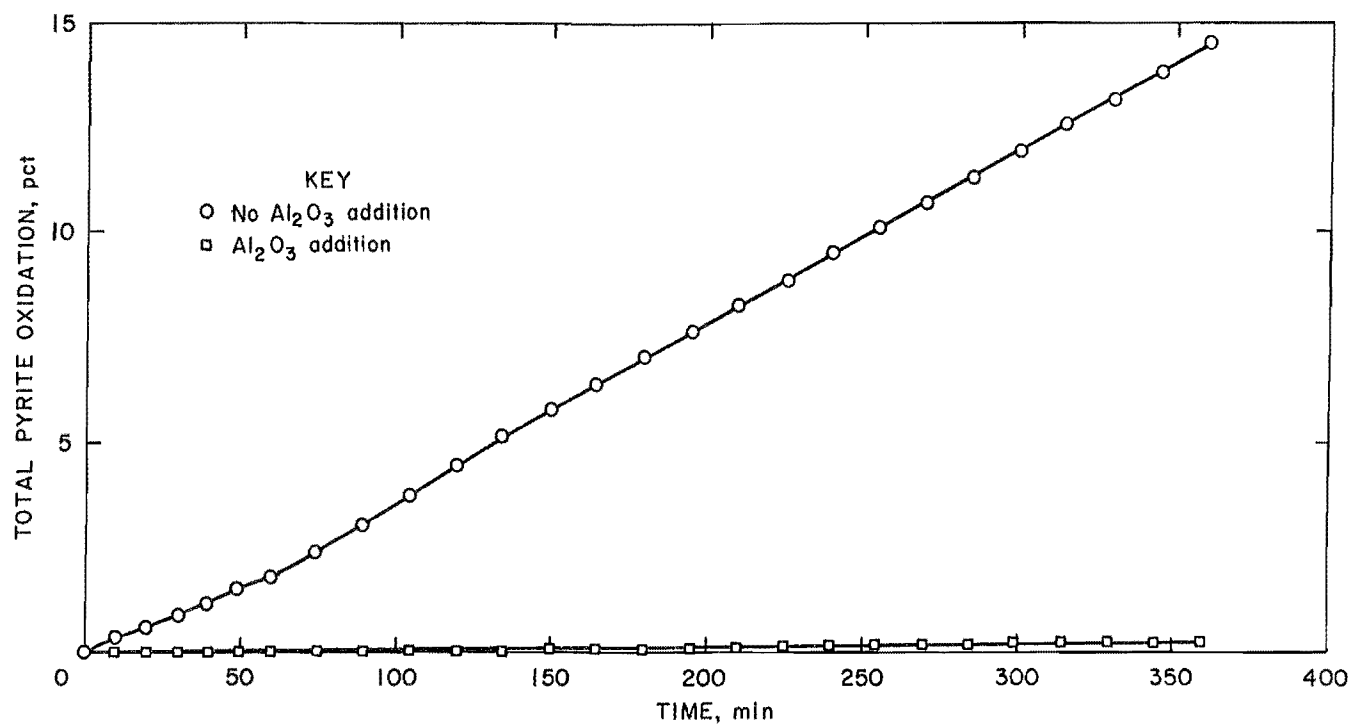
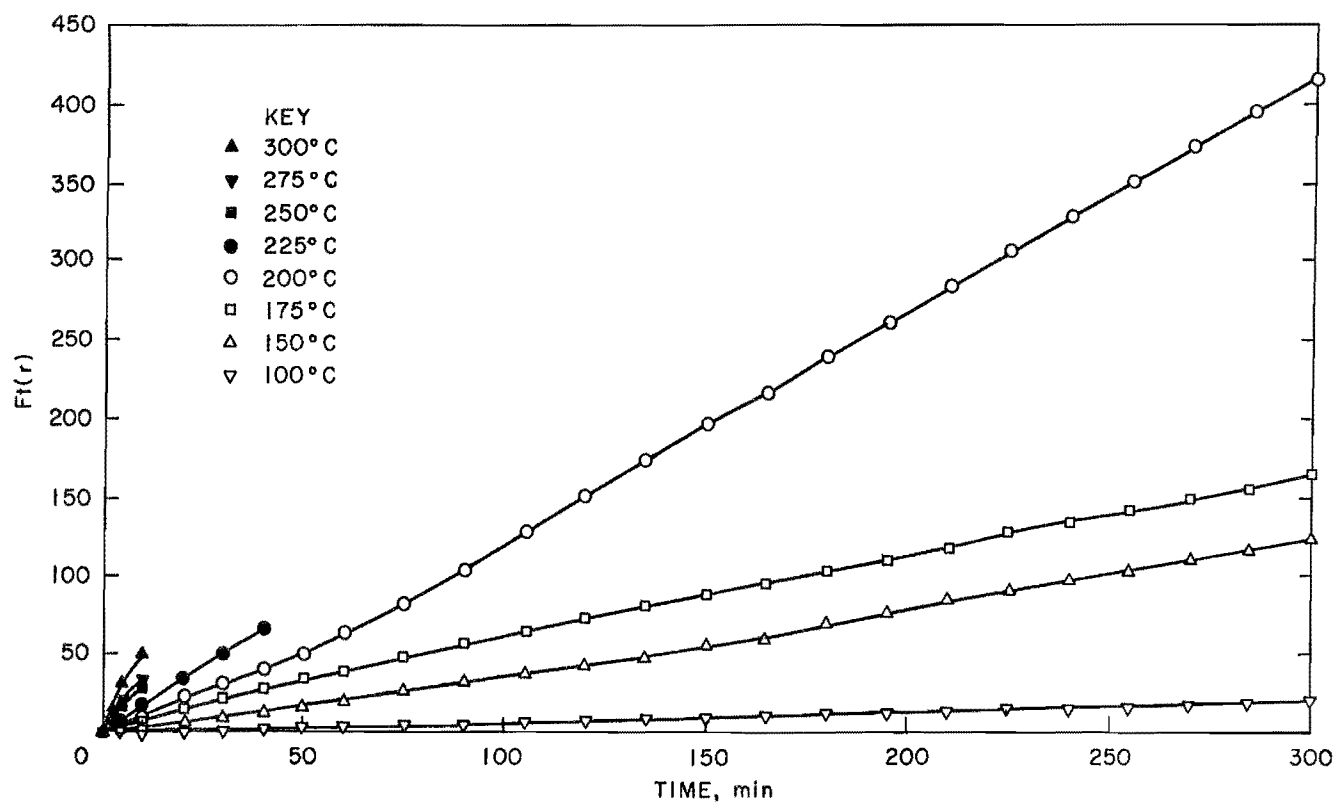


FIGURE 6.—Effect of activated alumina addition on pyrite oxidation.

FIGURE 7.—Variation of $F_1(r)$ with time.

topochemical mechanism for the low-temperature oxidation of pyrite. The slope of these plots gives a measure of the topochemical rate coefficient k at each of the test temperatures. Plots of $F_d(r)$ versus time were not linear and thus indicated that low-temperature pyrite oxidation is not diffusion controlled.

The temperature dependence of the rate constant k is given by the Arrhenius equation

$$k = e^{-\Delta Q/RT}, \quad (3)$$

where ΔQ is the activation energy, R is the ideal gas constant and T is the temperature of the reaction. Taking the natural log of both sides gives

$$\ln k = -\Delta Q/RT, \quad (4)$$

which can also be written as

$$\log k = -\Delta Q/(2.303)RT. \quad (5)$$

Figure 8 shows an Arrhenius-type plot of $\log k$ versus $1/T$, where T is the temperature of the reaction in kelvins (K). The slope of this plot is equal to $-\Delta Q/(2.303)R$. If R is 1.9872×10^{-3}

kcal/(mol·K), the activation energy is given by the following equation

$$\Delta Q = -(\text{Slope})(2.303)(1.9872 \times 10^{-3}), \quad (6)$$

and is in units of kcal/mol. Multiple points at a given temperature of oxidation were derived from different slopes of segments of the $F_d(r)$ versus t plots for these temperatures in figure 4. The activation energy for pyrite oxidation in an atmosphere of 40 vol pct O_2 and 60 vol pct water vapor was determined from the slope of this plot and found to be 8.9 kcal/mol pyrite. Considering that negligible oxidation is observed in the absence of water vapor even with 100 vol pct O_2 , at these temperatures the activation energy for pyrite oxidation in the absence of water vapor must be quite high. The low-activation energy for pyrite oxidation in the presence of 60 vol pct water vapor again indicates the importance of water vapor in the oxidation of pyrite, and that a lowering of the water-vapor content in the atmosphere is needed to decrease the rate of pyrite oxidation.

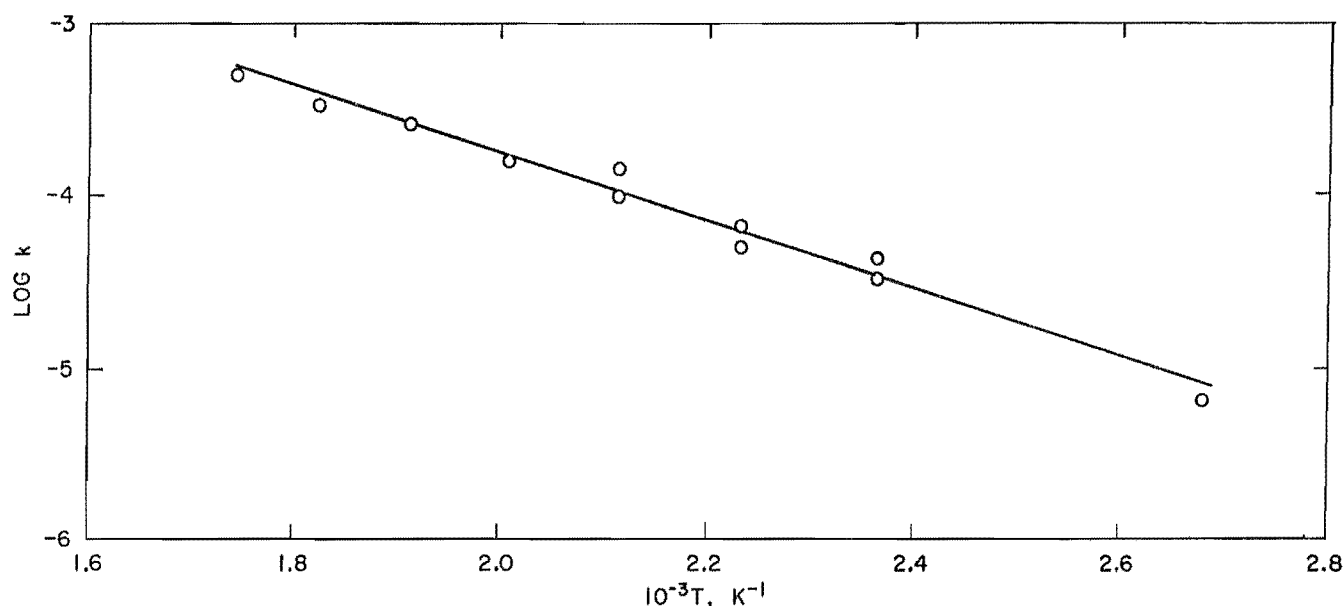


FIGURE 8.—Arrhenius plot for pyrite oxidation in an atmosphere containing 60 vol pct water vapor and 40 vol pct O_2 .

SUMMARY AND CONCLUSIONS

Although oxygen is needed for pyrite oxidation, water-vapor content of the atmosphere was found to be the critical factor in the rate of spontaneous oxidation of pyrite. The critical amount of water vapor in the atmosphere required for accelerated pyrite oxidation is about 20 pct. At or below this concentration, pyrite oxidation is very slow; while above this content, pyrite oxidation drastically increases with increasing water-vapor content. Without the presence of water vapor in the atmosphere, pyrite oxidation was negligible even in a pure-oxygen atmosphere. With the presence of water vapor, the rate of oxidation reached a maximum with 30 vol pct O_2 in the atmosphere.

The mechanism of low-temperature oxidation of pyrite was found to be topochemical. The adherence of the kinetics of pyrite oxidation to the contracting sphere model, and not a diffusion model, indicates that the oxidation process is controlled by the chemical reaction at the interface between the reactant (FeS_2) and product ($FeSO_4$) phases. An activation energy of 8.9 kcal/mol FeS_2 was obtained

for oxidation of 60 vol pct water vapor and 40 vol pct O_2 . The low-activation energy under these conditions suggests the importance of water as a catalyst in the oxidation of pyrite.

The rate of pyrite oxidation is also greatly affected by the particle size of pyrite being oxidized. The rate of pyrite oxidation is very slow for particle sizes above 40 μm ; however, for particle sizes below 40 μm , the rate of oxidation increases drastically with decreasing particle size. Room-temperature pyrophoric behavior was observed for an unoxidized, fine-ground pyrite sample (55 pct minus 5- μm material); however, a surface-oxidized, fine-ground pyrite sample (55 pct minus 5- μm material) had to be heated above room temperature before pyrophoric behavior was observed.

Mixing activated Al_2O_3 with pyrite drastically decreased the pyrite oxidation, while mixing of CaO with the pyrite resulted in an increase in pyrite oxidation. Water-adsorbing additives, if properly mixed with the pyrite, can decrease the rate of pyrite oxidation.

REFERENCES

1. Short, B. Magma Mine Fire. Min. Congr. J., v. 48, No. 9, Sept. 1962, pp. 42-45.
2. Baker, R. M., and J. Nagy. An Annotated Bibliography of Metal and Non-metal Mine Fires (contract JO295035, Allen Corp.). BuMines OFR 68(1-3)-81, 1980, 721 pp.; NTIS PB 81-233711.
3. Stevens, R. B. Improved Spontaneous Combustion Protection for Underground Metal Mines (contract HO282002, FMC Corp.). BuMines OFR 79-80, 1979, 264 pp.; NTIS PB 80-210461.
4. Ninteman, D. J. Spontaneous Oxidation and Combustion of Sulfide Ores in Underground Mines. A Literature Survey. BuMines IC 8775, 1978, 36 pp.
5. Stewart, R. W., A. P. Linden, I. B. Cutler, and M. E. Wadsworth. Geometric Factors in Solid-State Reactions. Ch. in Energetics in Metallurgical Phenomena, ed. by W. M. Mueller. Gordon and Breach, New York, 1967, v. 3, pp. 791-794.
6. McKewan, W. M. Kinetics of Iron Oxide Reduction. Trans. Metall. Soc. AIME, v. 212, 1958, pp. 791-794.